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CITRUS PECTIN

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PURPOSE OF INVESTIGATION

Lemon, orange, and grapefruit residue, thousands of tons of which are discarded each year at citrus by-product factories, consists principally of peel, pulp, and seeds. From 1.5 to 3 per cent of such residue, depending upon the ripeness of the fruit, is pectin, which occurs largely as pectose, an insoluble material, in the covering of the intercellular walls of the peel.

Pectin is a necessary constituent of jellies and marmalades. When any fruit lacks enough pectin to form a jelly, the quantity required to supply the natural deficiency may be added to the jelly stock. The principal source of commercial pectin used in this way has been apple pomace from vinegar factories, but, according to Will (*60*) [2] and Zoller (*61*), the possibilities of producing pectin from citrus fruit by-products are great. The simple method used in making apple pectin, which consists in dissolving out the pectin from the apple pomace with hot acidulated water and then concentrating it to a viscous sirup, can not be satisfactorily applied to citrus residues. The oils and bitter principle in citrus peel impart a disagreeable bitter taste to the product, making it necessary to either remove them or precipitate the pectin from the solution.

The properties of citrus pectin were studied in the Bureau of Chemistry and methods for its production on a commercial scale were evolved. The results of this work are reported in the following pages.

[1] E. M. Chace, chemist in charge, laboratory of fruit and vegetable chemistry, supervised the work here reported.

[2] Italic numbers in parentheses refer to the bibliography on p. 16. Not all of the articles there listed, however, are referred to in the text; several were published after the work here reported was completed.

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RESULTS OF PREVIOUS INVESTIGATIONS

Pectin was discovered in 1825 by Braconnot (*6*). Since then the chemistry of pectin and its related compounds has been the subject of extended research. Czapek (*18*), von Lippmann (*36*), Grafe (*1*), Beilstein (*4*), and Tollens (*50*) have summarized these investigations. Bigelow, Gore, and Howard (*5*) give a review, with an extended bibliography, of the work done up to 1905. More recently Ehrlich (*20*), Oden (*39*), and Fellenberg (*24*) have published work on this subject.

Confusion in designating substances of a pectinous nature has always existed. Fellenberg's exhaustive research helps to clarify the matter by giving the relations between the compounds. All pectinous materials are derived from pectose, or protopectin, an insoluble substance which forms the covering of the intercellular walls and middle lamella of unripe and some ripe, but no overripe, fruit. During the ripening of the fruit, pectose is converted into soluble pectin by the action of enzymes. This action may be produced also by boiling the fruit with water, the change occurring more rapidly when a weak organic acid solution is used. According to Fellenberg, this reversible colloid should have the formula $C_{78}H_{120}O_{68}$, not that of a true carbohydrate. Earlier investigators suggested formulas which also lack the number of hydrogen atoms requisite for a carbohydrate.

Pectin is closely related to starch and the plant gums and is usually classed as a polysaccharide. When mixed under certain conditions with sugar, acid, and water it produces a jelly and, with an excess of alcohol, precipitates from solution. As fruit rots, the pectin is changed to pectic acid by an enzyme (pectase), an action which also may be produced by treating pectin in the cold with dilute sodium hydroxide. Fellenberg found that methyl alcohol was split off during this change and since then Tutin (*51*) has shown that acetone is produced. Fellenberg considers pectin to be the methyl ester of pectic acid, containing eight carboxyl groups. Pectic acid is only slightly soluble in water and will not form a jelly with acid and sugar. Upon treatment with acids it breaks down into arabinose, galactose, galacturonic acid, and other compounds. Gaertner (*26*) found that sugar-beet marc contained a large proportion of pectose, which was converted into pectin upon boiling with water. From the pectin he obtained pectic acid and from the pectic acid, galactose and galacturonic acid. Weisberg (*56*) and Wilhelmj (*59*) have also worked with pectin from sugar beets. Carré (*12*) has shown that pectin in apples reaches a maximum during the process of ripening and gradually decreases as the fruit becomes overripe. These results show that only good sound fruit, not too ripe, should be used for the commercial production of pectin; in fact, unripe fruit is better.

METHODS FOR DETERMINATION OF PECTIN

The method of the Association of Official Agricultural Chemists for alcohol precipitate in fruits and fruit products (*2*) was not satisfactory in working with solutions which contained a large proportion of pectin, because gums and other alcohol-insoluble substances were

precipitated by the high percentage of alcohol used, and it was difficult to completely wash out the sugars, acid, and soluble material. Campbell's method (*10*) also requires a large excess of alcohol.

After many experiments, the following method was adopted: Filtered pectin solution (50 or 100 cc.) was added to 1½ volumes of 95 per cent alcohol, allowed to stand overnight, and filtered on a qualitative filter paper reinforced with a hard filter paper, using reduced pressure. The precipitate was washed with 100 cc. of 60 per cent alcohol, followed by about 200 cc. of 95 per cent alcohol, removed from the filter while wet, and dissolved in about 40 cc. of water. The solution was reprecipitated and washed as before, finally using a little ether. The precipitate was removed from the filter, dried in a water oven for 4 hours, weighed, ignited, and reweighed.

Although probably not as accurate as Fellenberg's pectic acid method (*23*) and the more recently published methods of Wichmann and Chernoff (*57*) and Carré and Haynes (*13*), the method was rapid and gave comparable results.

PRELIMINARY EXPERIMENTS

The literature contains many methods for the preparation of pectin in small quantities for the study of its chemical composition, but little on the details for commercial production. Many of the methods given produce pectic acid and related compounds instead of pectin (*54*). In a series of preliminary experiments, the methods of Hunt (*34*), Magoon and Caldwell (*38*), Schryver and Haynes (*43*), and Clayson, Norris, and Schryver (*15*) did not yield pectins suitable for making fruit jellies.

Vauquelin (*55*) in 1829 precipitated pectin from solution with alcohol, and Frémy (*25*) in 1840 produced powdered pectin with alcohol. Caldwell (*9*) concentrates the pectin solution by freezing and then precipitates it with alcohol.

The identity of the bitter principles in the peel of lemons and oranges grown in the United States is not well established. The glucoside naringin, found by de Vry (*58*) to be the bitter principle in grapefruit (*Citrus decumana*), does not occur in other citrus fruits. The bitter glucosides isohesperidin and aurantiamarin have been found in some varieties of orange by Tanret (*47*), while the nearly tasteless glucoside hesperidin is present in practically all citrus fruits except grapefruit (*49*). Attempts made to destroy the bitter principles in the pectin extracts by means of enzymes or to remove them with chemicals were unsuccessful. In making pure pectins several investigators have first washed the pectin-containing material, either before or after drying, with alcohol, acetone, and ether. This removes impurities, including the bitter principles from citrus residues, but requires a large quantity of solvent.

Pectin extracts were dialyzed in collodion sacs in several changes of cold water until all of the acid and bitter principle had dialyzed. Although about 90 per cent of the solids not pectin dialyzed, at least 50 per cent of the pectin passed through the membrane (Table 1).

TABLE 1.—*Composition of lemon pectin extracts before and after dialysis in collodion sacs*

Pectin	Composition				
	Total solids	Ash	Acid as citric	Pectin	Nonpectin solids
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*
Before dialysis	4.20	0.41	0.30	0.73	3.47
After dialysis:					
Sac 1	.77	.09	----------	.46	.31
Sac 2	.81	.04	----------	.35	.46
Sac 3	----------	----------	----------	.32	----------

Two lots of orange pectin extract were dialyzed in a small osmogene designed by Poore (*41*), using tap water heated to 75° C. Lot 1 (38 liters) was dialyzed for 168 hours, although the extract and tap water were in motion for only 45 hours. Lot 2 (72 liters) was dialyzed for 190 hours, with the extract and water in motion for 47 hours. The results are shown in Table 2.

TABLE 2.—*Composition of orange pectin extracts before and after dialysis in osmogene*

Pectin	Composition				
	Total solids	Ash	Acid as citric	Pectin	Non-pectin solids
Lot 1:	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
Before dialysis	6.49	0.38	0.27	0.97	5.52
After dialysis	1.83	.09	.06	.61	1.22
Lot 2:					
Before dialysis	2.53	.19	.15	.77	1.76
After dialysis	1.57	.13	.05	.51	1.06

Jellies made from the concentrated dialyzed extracts were poor in taste and appearance. The experiments showed that until a membrane less permeable to pectin and with a greater speed of dialysis for the other constituents is produced, the dialysis method will not be satisfactory. It is possible, however, that the electro-osmotic purification method of Schwerin (U. S. Patent 1,235,064), as applied to glue, gelatin, and other colloidal substances, would be practicable.

By agitating several 110-kilogram lots of finely-ground residue in running water under various conditions, it was possible to remove nearly all of the bitter principles. About half of the pectin dissolved, however.

If ethyl alcohol, one of the cheapest and best organic precipitants of pectin, is used, the pectin extract must be concentrated as far as practicable in order to avoid using too much. Powdered pectin was treated with alcohol of different strengths at room temperature for two days, and at 60° C. for two hours. At least 60 per cent alcohol by volume, or 54 per cent by weight, was necessary to precipitate all of the pectin from solution.

METHODS OF EXTRACTION

During the course of the work, the quantity of pectin obtained by extracting at different temperatures with solutions containing various percentages of citric acid was determined several times. The sample was heated with three times its weight of solution for two hours and filtered, and the residue was repeatedly extracted until only a trace of pectin was obtained, five or six extractions being sufficient. The jellying quality of the pectins varied decidedly, depending upon the treatment.

TABLE 3.—*Effect of acidity and temperature on quantity of pectin extracted*

Sample No.	Material	Weight of sample	Acidity of solution (citric acid)	Temperature	Pectin in material
		Grams	*Per cent*	*° C.*	*Per cent*
1	Peel from frozen lemons	650	0.02	98	1.53
2	Peel from frozen oranges	200	.02	98	1.28
3	Grapefruit peel	200	.02	98	1.48
4	Lemon residue	400	.02	98	1.95
5	Orange peel	200	.02	98	2.71
		200	.02	125	2.50
		200	.01	110	2.63
		100	.02	110	2.27
6	Orange residue	100	.06	98	2.73
7	Lemon peel	200	.21	98	2.54
		200	.64	98	3.64
8	Grapefruit peel	200	.01	98	2.36
		200	.39	98	4.08

The percentages of pectin in the samples analyzed (Table 3) depend largely upon the maturity of the fruit. Higher results would probably have been obtained on samples 1 to 6, inclusive, if the acidity of the solution had been increased.

A series of experiments on the extraction operation was made to determine the effect of temperature, time of heating, and acidity on the quantity and quality of the product. The following jelly test to determine the quality of pectin was adopted:

Thirty-one grams of sucrose was placed in a 150 cc. beaker with 19 cc. of distilled water and 0.25 gram of citric acid. The solution was brought to boiling, which in this case took 2½ minutes. The flame was then removed and a known weight of the dry pectin was dissolved in 6 cc. of water and added to the contents of the beaker. The solution was boiled gently for a minute. The beaker was then left overnight, after which the character of the jelly was noted.

If, according to Goldthwaite's standard (*28*), it was tender enough to cut easily and yet so firm that the angles produced retained their shape, and was not sirupy, gummy, sticky, or tough, it was considered a good jelly. Otherwise the test was repeated, using a different quantity of pectin.

As about 7 cc. of water evaporated during the test, the quantity of jelly obtained remained at a standard weight of about 50 grams. The rate of boiling and the quantity of water used should be regulated to give the standard weight. The weight of pectin used, divided by the weight of jelly obtained, gives the percentage of pectin required for a good jelly.

When dissolved in water, pectins of high-jellying quality produced a very viscous solution, while the inferior pectins showed only a slight viscosity. Check tests using two and four times the quantities of acid, pectin, etc., gave the same results.

Table 4 shows the results obtained by one extraction of five 370-gram samples of finely ground lemon peel, with a 0.1 per cent citric acid solution, varying the heating period.

TABLE 4.—*Results of a single extraction of lemon peel with 0.1 per cent citric acid, varying the time of heating*

Sample No.	Temperature	Time of heating	Pectin in peel	Pectin for a good jelly
	° C.	*Minutes*	*Per cent*	*Per cent*
1	98	15	0.73	0.3
2	98	45	1.24	.3
3	98	75	1.65	.4
4	98	120	2.10	.4
5	70	240	.84	.3

Table 5 gives the results of two 3-hour extractions of two 680-gram samples of lemon peel, varying the acidity.

TABLE 5.—*Results of two 3-hour extractions of lemon peel at 70° C., varying the acidity*

Sample No.	Extraction	Acidity (citric acid)	Pectin in peel	Pectin for a good jelly
		Per cent	*Per cent*	*Per cent*
1	First	0.09	0.23	0.5
1	Second	.04	.32	.5
2	First	.36	.46	.4
2	Second	.37	.57	.3

The results of two half-hour extractions of a 330-gram lot of lemon peel, using distilled and tap water, are given in Table 6.

TABLE 6.—*Results of two half-hour extractions of lemon peel with 0.5 per cent citric acid at 98° C., using distilled and tap water*

Sample No.	Extraction	Water	Pectin in peel	Pectin for a good jelly
			Per cent	*Per cent*
1	First	Distilled	1.07	0.2
1	Second	do	1.44	.3
2	First	Tap	1.20	.3
2	Second	do	1.23	.3

To ascertain the effect of low acidity on the quality of the product, a 1,950-gram lot and a 470-gram lot of orange peel were extracted twice at 98° C., with varying proportions of acid.

TABLE 7.—*Results of two three-quarter-hour extractions of orange peel at 98° C., varying the acidity*

Extraction	Acidity (citric acid)	Pectin in peel	Pectin for a good jelly
	Per cent	*Per cent*	*Per cent*
Lot 1:			
First	0.03	0.43	0.60
Second	.01	1.16	2.20
Lot 2:			
First	.29	.90	.31
Second	.10	1.60	.34

The results up to this point indicated that an hour's heating of the peel at 98° C. in three times its weight of slightly acid solution (at least 0.1 per cent) yielded a fair quantity of good-quality pectin. Samples 1 to 5, inclusive, of the pectins shown in Table 3 were of poor quality, because of the low acidity. There was no advantage in extracting the pectin above the simmering temperature of 98° C. The finer the peel, the more readily the pectin was removed.

In order to determine the proper acidity and feasible number of extractions, 1,800 grams of finely ground lemon peel was divided into eight lots of 225 grams each and extracted twice for 45 minutes at 98° C. Additional extractions were made on samples 3 and 6. All of these results are given in Table 8.

TABLE 8.—*Results of two three-quarter-hour extractions of lemon peel at 98° C., varying the acidity*

Sample No.	Acidity (citric acid)	Pectin in peel	Pectin for a good jelly
	Per cent	*Per cent*	*Per cent*
1	0.02	1.92	1.33
2	.12	.98	.25
3	.21	1.22	.25
	.21	1.32	.60
4	.30	1.46	.25
5	.44	1.69	.25
6	.64	2.26	.25
	.64	1.38	1.70
7	.88	2.18	.25
8	1.20	2.71	.35

Two 200-gram samples of one lot of lemon peel were heated three times at 98° C. with 0.4 per cent acid, one sample for 60 and the other for 90 minutes. The results are shown in Table 9.

TABLE 9.—*Results of three extractions of lemon peel at 98° C. with 0.4 per cent citric acid*

Sample No.	Extraction	Time of heating for each extraction	Pectin in peel	Pectin for a good jelly
		Minutes	*Per cent*	*Per cent*
1	First and second	60	2.52	0.25
1	Third	60	.83	.51
2	First and second	90	2.96	.34
2	Third	90	.79	.68

Two 200-gram samples from 1,300 grams of grapefruit peel were extracted twice at 98° C. for an hour, varying the acidity. The results are shown in Table 10.

TABLE 10.—*Results of two 1-hour extractions of grapefruit peel at 98° C., varying the acidity*

Sample No.	Acidity (citric acid)	Pectin in peel	Pectin for a good jelly
	Per cent	*Per cent*	*Per cent*
1	0.02	1.17	0.86
2	.34	1.95	.41

Although a good yield of pectin is obtained in two extractions with 0.02 per cent acid, the jellying quality of such pectin is poor. Pectins of much higher jellying quality are obtained when at least 0.1 per cent of acid is present in the solution, and the quantity extracted increases with the increase of acid. After two extractions, the pectin is of inferior jellying quality. A third extraction yields enough pectin to warrant the extra cost if it were not of a poorer quality, but the fourth and fifth extractions are not of economic value. It is believed that 0.3 to 0.6 per cent acid is enough to produce pectin of good quality in two extractions of one hour each, and that possibly tartaric acid and other organic acids can be used. Although a little more pectin is obtained by heating for one and one-half hours, the quality of the product is not quite so good.

PREPARATION OF CONCENTRATED SOLUTIONS AND POWDERED PECTIN

The concentrated extracts are bitter, and jellies made from them, containing as little as 0.25 per cent pectin, although of good consistency, have a slightly bitter taste. The concentration of pectin extract for the production of a satisfactory solid product was studied.

One hundred and sixty kilograms of pectin solution was obtained from 91 kilograms of lemon residue by two extractions. Bakers' yeast was added, and the mixture was allowed to ferment for four days at about 30° C. It was than clarified by adding 3 per cent by weight of kieselguhr, boiling, and filtering. As kieselguhr removes little pectin, if any, and is the best clarifying medium of those tried, it was used throughout the work.

Although the pectin was not destroyed by the fermentation, its jellying quality was impaired Thirty kilograms of the fermented extract was concentrated to 5.5 kilograms by freezing and centrifuging three times. After experimenting with a 40-gallon silver-lined vacuum pan and a small medicinal type atomizer, a spraying apparatus that produced about 50 grams of a very fine, light-colored powder at a temperature in the pan of 54° C. was arranged. The product thus obtained was very bitter; but, after extraction in a Soxhlet apparatus with 95 per cent alcohol, a lighter-colored powder without a trace of bitter taste was obtained. The composition of the solutions and the powder is given in Table 11.

TABLE 11.—*Composition of pectin solution and powder made in the laboratory*

Product	Composition				
	Total solids	Ash	Acid as citric	Total sugar as invert	Pectin
Pectin solution:	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
Original	3.31	----------	0.38	0.80	0.82
After fermentation	2.24	----------	.35	.13	.80
After concentration	12.49	0.88	1.80	----------	4.20
Pectin powder:					
Original	94.95	7.12	14.40	----------	31.00
After alcohol extraction	89.10	9.81	6.90	----------	44.70

From another lot of lemon residue, 38 kilograms of concentrated extract was made by freezing. This was shipped to a powdered-milk company, which returned about 1,300 grams of very bitter powder, stating that the material could be dried satisfactorily by their process, but that much had been lost in their apparatus. An analysis of this powder showed the following results:

Moisture (per cent)	3.62
Acid as citric (per cent)	6.75
Pectin (per cent)	43.7
Alcohol precipitate (per cent)	52.9
Protein (per cent)	5.28
Ash (per cent)	9.14
Water-soluble ash (per cent)	4.19
Alkalinity of water-soluble ash (cc. 0.1 *N* hydrochloric acid per gram)	4.5
Alkalinity of water-insoluble ash (cc. 0.1 *N* hydrochloric acid per gram)	6.3
Reducing sugars (per cent)	Trace.
Soluble P_2O_5 (per cent)	None.
Insoluble P_2O_5 (per cent)	0.40
P_2O_5 in ash (per cent)	4.3

Apparently concentrated pectin solutions can be powdered and then extracted with a suitable solvent to yield a satisfactory product. A 60 per cent alcohol, denatured with benzol, methyl alcohol, or ethyl acetate, can be employed, if care is taken to thoroughly remove the denaturant when drying.

As the spraying process is expensive and as the work previously conducted indicated that alcohol was the most suitable substance for the precipitant and the washing material, an effort was made to devise a process employing as little of the reagent as possible. Upon adding a viscous sirup of pectin to 1½ volumes of 95 per cent alcohol, a heavy gelatinous mass was thrown down. This mass could be freed from the solution by pressing or centrifuging, but it could be washed only with difficulty. Upon dissolving the unwashed pectin in water and distilling off the alcohol, however, a pectin concentrate having only a slightly bitter taste can be produced.

If the pectin extract is evaporated to dryness, it becomes tough and brittle and sticks to the container. After reduction to a fine powder, great difficulty was experienced in removing the bitter taste with hot 60 per cent alcohol.

It finally became evident that if the pectin solution was concentrated to a thick paste, containing from 25 to 50 per cent of solids, a minimum quantity of alcohol would remove the bitter substance

and combine with the paste to form a granular nongelatinous mass, from which the solvent could be removed by pressure before drying. A continuous system of washing and a constant temperature of about 60° C. were advantageous for large quantities of the paste. The best temperature for concentrating the pectin solution was 60° C. Much higher temperatures impair the jellying power of the pectin and give a dark product. As a preliminary treatment the freshly ground residue or peel was soaked overnight in three of four times its weight of water, the excess of which was poured off. In this way much of the bitter matter and of the color, but only a trace of pectin, was removed.

The results obtained by using 60 per cent ethyl alcohol in preparing pectin paste were compared with those obtained by using 60 per cent ethyl alcohol denatured with 5 per cent methyl alcohol, ethyl acetate, and benzol, respectively, in the following experiment:

Four hundred cubic centimeters of pectin extract containing 0.02 per cent acid, and therefore of low jellying power, was precipitated with 60 per cent alcohol, washed, and dried. Forty-five hundred cubic centimeters of the same extract was evaporated below 60° C. to 360 grams of paste, which was divided into four parts, placed in Erlenmeyer flasks, heated for an hour at 60° C. with 200 cc. of the mixtures listed in Table 12, and dried.

TABLE 12.—*Effect of denatured alcohol in preparation of pectin*

Sample No.	Treatment	Dried material	Pectin		
			In dry material	Calculated to be in original extract	Required for a good jelly
		Grams	*Per cent*	*Per cent*	*Per cent*
1	Precipitated with ethyl alcohol	2.21	70.0	0.39	0.4
2	Paste; ethyl alcohol	7.34	57.0	.37	.5
3	Paste; ethyl alcohol and 5 per cent methyl alcohol	7.47	64.8	.43	.5
4	Paste; ethyl alcohol and 5 per cent ethyl acetate	7.30	66.3	.43	.5
5	Paste; ethyl alcohol and 5 per cent benzol	7.22	59.3	.38	.5

As the quantity of pectin, calculated from the dry matter of the original extract, was within the experimental error for each of the alcoholic mixtures, the results show that the denatured alcohols are as suitable for purification as ethyl alcohol. The jellying power of the pectin in the paste was only slightly affected by the concentration and washing.

Several lots of pectin were made by the following method: The pectin solution was concentrated to a thick paste (from 25 to 50 per cent solids) and washed with alcohol denatured with benzol. Although the facilities in the laboratory did not permit the production of pectin on a large scale, this method is here proposed for use on the commercial scale. The operation on one lot was as follows: Thirty liters of water was added to 8.6 kilograms of finely ground peel from slightly green lemons, and, after remaining on the peel overnight, was pressed out. The residue was heated twice for an hour at 98° C., with 25 liters of water containing 0.4 per cent of citric acid. The 47 liters of extract obtained was filtered, using 2 per cent of kieselguhr.

For comparison, three liters of the filtrate was precipitated with one and one-half volumes of 95 per cent alcohol in the usual way and washed, using the equivalent to 5,500 cc. of 95 per cent alcohol. This gave 16.4 grams of crude pectin.

Twenty-nine liters of the same filtrate was evaporated in small lots on the steam bath below 60° C. in a strong current of air to a paste weighing 2,200 grams and containing 25 per cent of total solids. Calculation showed that about 3,300 cc. of 95 per cent alcohol would be required to combine with the water present in the paste and form a 60 per cent alcohol mixture. The following method was used for purification: 1,300 cc. of 95 per cent alcohol containing 5 per cent benzol was added to the paste and stirred, and after a short time the alcohol was absorbed. The granular mass produced was divided into four parts and placed in Erlenmeyer flasks. To each of two of the flasks 500 cc. of 95 per cent alcohol was added and the whole was heated to 60° C. The washings were pressed out and added to the other two flasks, with an additional 1,000 cc. of alcohol. These flasks were heated to 60° C., and the washings were pressed out and set aside. Meanwhile 900 cc. of 60 per cent alcohol was added to one of the flasks and heated to 60° C. The washings were pressed out and added to the other flasks in rotation and the heating was repeated. Then 600 cc. of 60 per cent alcohol was added in rotation and heated. By this means only 4,200 cc. of 95 per cent alcohol were required, as compared with 5,500 cc. used in the precipitation of about one-tenth as much pectin extract.

The washed material was dried below 70° C. and finally placed in the water oven. One hundred and ninety-two grams were obtained. The pectins were then ground and examined, with the results shown in Table 13.

TABLE 13.—*Composition of precipitated and washed pectins*

Pectin	Composition			
	Total solids	Ash	Acid as citric	Pectin
	Per cent	*Per cent*	*Per cent*	*Per cent*
Original extract	1.97	0.11	0.42	0.48
Precipitated material [1]	88.20	1.81	.40	85.80
Washed material [2]	94.65	7.77	8.10	66.30
Removed by washing	66.00	53.00	88.00	9.00

[1] Quantity required for a good jelly, 0.4 per cent; actual pectin, 0.3 per cent.
[2] Quantity required for a good jelly, 0.8 per cent; actual pectin, 0.5 per cent.

Although the jellying power of the washed sample is less than that of the precipitated sample, owing no doubt to the length of time required to evaporate the solution on the steam bath, this pectin may be graded as fair. On a large scale, the evaporation could be made in a vacuum pan, or better, on a revolving steam drum or some similar arrangement, where a little solution is rapidly evaporated to a paste. Thus, using a continuous counter-current washing device, a minimum quantity of 95 per cent alcohol would be required to unite with the water in the paste and form a 60 per cent alcoholic solution. The alcohol and also the acid can be recovered from the washings.

COMPOSITION OF APPLE, LEMON, AND ORANGE PECTINS

Samples of lemon and orange pectins, obtained by double alcoholic precipitation, and a sample of apple pectin, obtained by washing apple pomace three times with boiling alcohol and precipitating the water extract with alcohol containing hydrochloric acid, were analyzed by E. K. Nelson, of the Bureau of Chemistry. The alcohol precipitate and pectic acid were determined by the method of Wichmann and Chernoff (*57*), and the calcium pectate by the Carré-Haynes method (*13*), while the Zeisel method was employed for the methoxy number. The methods of the Association of Official Agricultural Chemists were used for determining the araban and galactan. The results are given in Table 14.

TABLE 14.—*Composition of pectins*

Pectin	Composition										Specific rotation
	Moisture	Ash	Acidity	Sodium hydroxide required for cold hydrolysis	Alcohol precipitate	Pectic acid	Calcium pectate	Methoxy number	Araban	Galactan	
	Per cent	*Per cent*	*Grams NaOH per 100 grams*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Degrees*
Apple	1.12	0.70	3.86	14.10	96.72	63.86	98.00	10.90	39.68	65.56	+210
Lemon	3.64	5.42	3.86	13.58	89.90	62.76	96.80	10.26	39.12	58.92	+206.5
Orange	8.14	5.90	1.00	12.06	81.76	54.80	84.60	8.85	34.96	56.08	+175
Calculated to alcohol-precipitate (pure pectin) basis											
Apple	------	------	3.99	14.57	--------	66.02	---------	11.27	41.02	67.78	+217.1
Lemon	------	------	4.29	15.10	--------	69.81	---------	11.41	43.51	65.54	+229.7
Orange	------	------	1.22	14.75	--------	67.02	---------	10.82	42.76	68.59	+214

The apple pectin is much purer than the citrus pectins. When calculated back to the pure pectin basis, however, no great differences were noted in the chemical composition, and no hope of being able to distinguish between them chemically is indicated.

PROPORTIONS OF ACID, SUGAR, AND CITRUS PECTIN NECESSARY TO PRODUCE JELLIES

Goldthwaite (*27*) studied the proportions of sugar and acid and the quantities of invert sugar produced in making fruit juice jellies, but paid little attention to the percentages of pectin actually present. Cruess and McNair (*16*) found that with a 1 per cent solution of orange pectin, a concentration of 0.3 per cent acid is necessary to give a firm jelly. Singh (*44*) studied the relations of pure citrus pectin, pure citric acid, and sugar in detail, but evidently used a pectin of poor jellying power, as a minimum of 0.9 per cent was required to jelly. He states that to prepare the pectin solution commercial powdered citrus fruit pectin was leached in boiling water and filtered through felt, four extractions being made. Possibly the lack of acidity in the extracting solutions yielded a pectin of low

jellying power. Barker (*3*) states that pectin must be present in quantities of 0.5 per cent or more to give a good cider apple jelly. Tarr (*48*) found a direct relation between jelly formation and active acidity of hydrogen-ion concentration, which can not be correlated with total acidity. The minimum hydrogen-ion concentration at which jelly formation occurred was pH 3.46.

By the standard test used throughout this work for determining the jellying quality of the citric acid pectins obtained (p. 5), it was found that 0.20 per cent pectin in the finished product gave a good jelly in one instance and 0.25 per cent in several other instances. In order to determine the variations in citric acid and sugar that could be used with the better grades of pectin, a large number of tests were made by this standard-jelly test.

Six pectins of high-jellying quality were obtained from three lots of lemon peel as follows: No. 1, from peel No. 1, by extracting for 45 minutes at 98° C. in 0.1 per cent acid solution; No. 2, from peel No. 1, by extracting for 15 minutes at 98° C. in 0.1 per cent acid solution; No. 3, from peel No. 1, by extracting for 4 hours at 70° C. in 0.1 per cent acid solution; No. 4, from peel No. 2, by extracting for 30 minutes at 98° C. in 0.1 per cent acid solution; No. 5, from peel No. 3, by extracting for 45 minutes at 98° C. in 0.1 per cent acid solution; No. 6, from peel No. 3, by extracting two samples twice for 45 minutes, one in 0.1 per cent acid solution and the other in 0.5 per cent acid solution, and then combining the two. The pectins were precipitated from solution twice with alcohol, washed, dried, and ground.

The effect of using varying quantities of citric acid with 0.26 per cent of pectin 1, 2, 3, and 4 was tested. The results are shown in Table 15. All of the percentages are based on the finished jelly.

A good jelly was obtained with as little as 0.045 per cent of acid. The 0.5 per cent acid jelly was considered the best tasting and enough of the sucrose (about 65 per cent) was inverted to prevent crystallization.

TABLE 15.—*Effect of variation of acid on consistency of jelly (pectin and sucrose nearly constant)*

Sample No.	Citric acid	Consistency of jelly	Sample No.	Citric acid	Consistency of jelly
Pectin 1:	*Per cent*		Pectin 2:	*Per cent*	
1	0.000	Sirup.	1	0.027	Sirup.
2	.020	Do.	2	.035	Do.
3	.040	Barely jellied.	3	.039	Do.
4	.045	Good jelly.	4	.046	Do.
5	.052	Do.	5	.048	Good jelly.
6	.080	Do.	6	.049	Do.
7	.100	Do.	Pectin 3:		
8	.200	Do.	1	.020	Sirup.
9	.300	Do.	2	.046	Fair jelly.
10	.400	Do.	3	.073	Good jelly.
11	.500	Do.	Pectin 4:		
12	.600	Do.	1	.020	Sirup.
13	.750	Do.	2	.043	Do.
14	.900	Do.	3	.046	Do.
15	1.300	Do.	4	.056	Fair jelly.
16	1.800	Do.	5	.065	Good jelly.
17	2.500	Do.	6	.073	Do.

Standard-jelly tests on pectin 5 and 6 were next made, using 0.5 per cent of acid, 0.25 per cent of pectin, and various quantities of sucrose. The water was either increased or decreased, so that the final jelly weighed about 50 grams. The results are noted in Table 16.

TABLE 16.—*Effect of variation of sucrose on consistency of jelly (acid and pectin nearly constant)*

Sample No.	Sucrose	Consistency	Sample No.	Sucrose	Consistency
Pectin 5:	*Per cent*		Pectin 6:	*Per cent*	
1	40.0	Sirup.	1	35.6	Sirup.
2	43.5	Fair jelly.	2	39.1	Do.
3	48.9	Good jelly.	3	43.5	Barely jellied.
4	53.2	Do.	4	46.8	Fair jelly.
5	54.9	Do.	5	50.0	Good jelly.
6	62.5	Do.	6	53.1	Do.
7	63.2	Do.	7	56.0	Do.
8	64.0	Do.	8	60.0	Do.
9	65.3	Fair jelly.	9	65.3	Fair jelly.
10	66.0	Do.	10	68.0	Do.
11	68.6	Do.	11	70.6	Barely jellied.
12	74.5	Very viscous sirup.	12	74.5	Very viscous sirup.
13	80.0	Do.	13	76.9	Do.

Further tests were made with pectin 6, increasing the quantity of pectin. The results are shown in Table 17.

TABLE 17.—*Effect of variation of pectin and sucrose on consistency of jelly (acid nearly constant)*

Sample No.	Pectin	Sucrose	Consistency	Sample No.	Pectin	Sucrose	Consistency
	Per cent	*Per cent*			*Per cent*	*Per cent*	
1	0.43	40.0	Sirup.	12	0.60	69.4	Very viscous sirup.
2	.43	43.5	Barely jellied.	13	.77	40.0	Sirup.
3	.43	46.8	Good jelly.	14	.77	41.6	Good jelly.
4	.43	62.5	Do.	15	.77	52.5	Fair jelly.
5	.43	64.0	Fair jelly.	16	.77	64.0	Barely jellied.
6	.43	68.0	Very viscous sirup.	17	.93	34.8	Sirup.
7	.60	38.3	Sirup.	18	.93	36.7	Do.
8	.60	40.8	Good jelly.	19	.93	40.9	Good jelly.
9	.60	46.8	Do.	20	.93	42.1	Do.
10	.60	51.4	Do.	21	1.11	37.5	Sirup.
11	.60	57.1	Barely jellied.				

The results in Table 16 show that the jellies produced were good when they contained between 50 and 65 per cent of sucrose, but the consistency of jellies having more or less than these proportions was poor. If the percentage of pectin is gradually increased to 0.93, the proportion of sugar necessary for good jelly decreases to about 41 per cent as a lower limit and to about 52 per cent as an upper limit. (Table 17.)

The results of varying all three of the jelly constituents in pectin 6 are given in Table 18. Increasing the acid or pectin within reasonable limits above those noted in the tables will not decrease the proportion of sugar required. With a definite proportion of pectin there is only a small decrease in sugar as the acid is increased.

TABLE 18.—*Effect of variation of pectin, acid, and sucrose on consistency of jelly*

Sample No.	Pectin	Citric acid	Total sugar as sucrose	Consistency	Sample No.	Pectin	Citric acid	Total sugar as sucrose	Consistency
	Per cent	*Per cent*	*Per cent*			*Per cent*	*Per cent*	*Per cent*	
1	0.26	0.82	39.1	Sirup.	14	0.60	1.07	40.0	Sirup.
2	.26	.82	43.0	Barely jellied.	15	.60	1.07	43.0	Good jelly.
3	.26	.82	47.8	Fair jelly.	16	.60	1.51	34.8	Sirup.
4	.26	1.07	39.1	Sirup.	17	.60	1.51	40.0	Good jelly.
5	.26	1.07	45.8	Fair jelly.	18	.77	.82	39.1	Barely jellied.
6	.26	1.51	47.8	Do.	19	.77	1.07	39.1	Good jelly.
7	.43	.82	39.1	Sirup.	20	.77	1.51	35.5	Sirup.
8	.43	.82	43.0	Good jelly.	21	.93	.82	39.1	Good jelly.
9	.43	1.07	40.0	Sirup.	22	.93	1.07	35.5	Sirup.
10	.43	1.07	43.0	Good jelly.	23	.93	1.51	34.8	Do.
11	.43	1.51	39.1	Sirup.	24	1.11	1.07	32.6	Do.
12	.60	.82	38.3	Do.	25	1.11	1.13	36.4	Good jelly.
13	.60	.82	43.0	Good jelly.	26	1.11	1.51	33.3	Sirup.

In making jellies with orange juice much less inversion of the sucrose was obtained than when working under like conditions with equivalent quantities of acid and pectin solutions, owing to the presence in the juice of inorganic salts, which, as noted by Browne (*8*), will diminish the inversion velocity of the acid. A sample of orange jelly stock containing 0.27 per cent of ash was jellied by the standard test (boiling for 1 minute) and also by boiling for 5, 10, and 15 minutes. The pectin was then precipitated from some of the jelly stock and redissolved in enough distilled water to give the original concentration of pectin, and the jelly test was made. The pectin-free stock and a solution of the ash after being made up to their original concentration were then given the standard jelly test. The results are shown in Table 19.

TABLE 19.—*Effect of mineral matter of orange juice on inversion of sucrose*

Sample No.	Material	Citric acid	Invert sugar
	Original stock solution:	*Per cent*	*Per cent*
1	Boiled 1 minute	0.52	10.87
2	Boiled 5 minutes	.55	19.02
3	Boiled 10 minutes	.53	25.58
4	Boiled 15 minutes	.54	35.87
	Precipitated pectin solution:		
5	Boiled 1 minute	.46	32.61
6	Boiled 5 minutes	.48	50.27
	Stock solution freed of pectin:		
7	Boiled 1 minute	.51	11.41
8	Boiled 5 minutes	.54	18.66
	Solution of ash:		
9	Boiled 1 minute	.43	10.33
10	Boiled 5 minutes	.49	19.02

HOW TO MAKE CITRUS JELLIES AND MARMALADES

As a result of the work here reported, a rapid and dependable method for making orange jellies and marmalades on a large scale, which standardizes the product as to color and consistency, has been developed. This method is described in Department of Agriculture Circular 232, "By-products from citrus fruits."

SUMMARY

The properties of citrus pectin and methods for its production were studied.

The dialysis of pectin extracts in an osmogene containing collodion-impregnated cloth membranes removed most of the bitter principles, but the dialysis was too slow and about one-third of the pectin dialyzed.

The best method of extraction was to heat the finely ground peel or residue with acidified water and clarify the expressed extract with kieselguhr.

The bitter principle was removed with alcohol from powdered pectin prepared from concentrated solutions of pectin in the laboratory and in a commercial plant.

A process whereby the pectin extracts are concentrated to a paste and washed by a continuous system with a minimum quantity of denatured alcohol was devised.

Little hope is indicated of distinguishing chemically between lemon, orange, and apple pectins; the composition, when calculated to the alcohol-precipitate basis, is much the same for each product.

A standard jelly test for determining the quality of the pectins produced throughout the investigation was developed.

The proportions of citric acid, sugar, and citrus pectin required to give good jellies were determined. The lower limit in the finished jelly for citric acid was 0.045 per cent, for pectin 0.20 per cent, and for sucrose 37 per cent.

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